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FIRST QUARTERLY REPORT

DEVELOPMENT OF HIGH ENERGY DENSITY
PRIMARY BATTERIES 200 WATT HOURS
PER POUND TOTAL BATTERY WEIGHT MINIMUM

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1. SUMMARY

The lower esters were evaluated as possible electrolyte solvents for lithium-anode primary cells. Conductivity-concentration data with LiClO_4 electrolyte were obtained for five solvents. The highest conductivity was recorded for a 3.0 M solution of LiClO_4 in methyl formate, which had the value of $3.2 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. In general, the maximum conductivity of LiClO_4 solutions decreased with increasing molecular weight of the solvent.

The stability of lithium metal in the esters and in solutions of LiClO_4 in the esters was studied. With the solvent alone, n-butyl formate appeared completely inert; and only very slow gassing was observed with methyl formate and methyl acetate. In the case of the last two solvents, a white film could be observed on the Li surface after five days of exposure. With LiClO_4 solute, n-butylformate gave a rapid reaction; and the reaction with methyl acetate was also accelerated; no difference in behavior was observed in the methyl formate tests between presence and absence of the solute.

Cell tests with several types of electrode construction and a number of electrochemical systems were performed. Modifications to the carbon-paper cathode construction were undertaken; also, electrodes having plastic binders for the active material were studied. The effect of these modifications was not fully evaluated in the presence of large variability in performance between replicate cells.

In testing cells having balanced theoretical electrode capacities, the system Li/CuF_2 with methyl formate - LiClO_4 electrolyte showed the best performance with respect to energy density, the highest

figure obtained being 130 watt hours per pound at the 40-hour rate. In general, electrochemical efficiencies of the cathode were in the range of 50 to 70 per cent with methyl formate electrolyte solvent, while those with butyrolactone were generally in the range of 20 to 30 per cent.

Of the other systems studied, Li/MnO_2 showed ability to discharge after a two-week open-circuit stand with butyrolactone - LiClO_4 electrolyte. The potential usefulness of this system appears to be limited by the failure of the material to reduce to the +2 state in the electrolytes employed.

2. INTRODUCTION

The purpose of this program is to develop a primary battery system having a minimum energy density of 200 watt hours per pound. The present report describes the activity and test results obtained during the first three months of the current program.

In view of the high energy density requirement for the system, only electrode materials having low equivalent weights can be considered. On the basis of earlier test results reported by this laboratory and other investigators, lithium appears to be the most promising anode reactant; although other possible materials, such as calcium, have not been extensively investigated. The strong reducing action of the metallic lithium dictates the use of aprotic electrolyte solvents in the system. Numerous electrolyte systems have been studied by this contractor under the preceding program (NAS 3-2775, Final Report No. CR-54083) by measuring their conductivity and decomposition potential.

Several cathode materials have been considered for use in a high energy density system. The heavy metal halides possess a sufficiently high theoretical energy density to warrant their consideration as the cathode active materials. A cell consisting of lithium negatives and copper fluoride positives can be calculated to possess a theoretical capacity of 211 ampere hours per pound of the active materials. In some solvents, such as butyrolactone, the potential of the couple has been observed to be in the range 3.3 to 3.5 volts. Assuming an operating voltage of 3.0 volts, the theoretical energy capability of the system can be calculated to be 3.0×211 , or 633

watt hours per pound. For an energy density of 200 watt hours per pound, an overall efficiency of $(200 \times 100)/633$, or 32 per cent, would be required. On the basis of performance of other primary systems, (see the Appendix), some of which are not necessarily designed for high energy density, this figure does not appear to be out of reach. In view of this, a substantial portion of the present effort was concentrated on studying the performance of the Li-CuF₂ couple. It was recognized, however, that cathode materials giving higher theoretical energy contents are highly desirable, provided that their kinetic properties are acceptable. Therefore, the search for other cathode materials was continued during the quarter (a source of alkali metal superoxides was located).

3. DISCUSSION OF EXPERIMENTAL WORK

3.1. ELECTROLYTE SYSTEM STUDIES

In order to be considered for the construction of high energy density, lithium-anode primary cells, an electrolyte solvent must satisfactorily meet several requirements, among which stability in the presence of a lithium metal anode and a cathode material such as CuF_2 , a suitable liquid range, and formation of sufficiently conductive solutions with stable electrolytes appear to be of prime importance. Other properties, such as low viscosity, low dissolution of cathode materials, low affinity for water, and compatibility with common materials of construction appear to be highly desirable.

In selecting candidate solvents, several criteria are useful and are, in general, available in the literature for the more common materials; these criteria include the structural formula (indication of the degree of aproticity), liquid range, molecular dipole moment and dielectric constant, and solubility in water. Some data for the lower esters are presented in Table I.

TABLE I
Physical Properties of Some Esters

<u>Ester</u>	<u>Sp.Gr.</u>	<u>M.P.</u>	<u>B.P.</u>	<u>Dielectric Constant</u>	<u>Solubility, grams per 100 ml of H_2O</u>
Methyl Formate	0.98	-99°C	+ 31°C	8.5	30.4 at 20°
Ethyl Formate	0.92	-80°	+ 54°	7.1	11.8 at 25°
Methyl Acetate	0.93	-98°	+ 57°	6.7	31.9 at 20°
Ethyl Acetate	0.90	-84°	+ 77°	6.0	8.6 at 20°
n-Butyl Formate	0.91	-90°	+107°	6.4	sl. s
Butyl Butyrate	0.87	-91°	+166°		sl. s
Ethyl Acetoacetate	1.02	<-80°	+180°	15.7	14.3 at 16°

Tests described in the following sections were performed with either "spectroquality" reagents as received (the lower esters), or with liquids dried by agitation with CaO for a period of at least three days. The solutes were obtained in the anhydrous condition from the manufacturer and were used as received.

3.1.1. Conductivity of Solutions of LiClO_4 in the Lower Esters

Conductivity-concentration data were obtained for solutions of LiClO_4 in five of the lower esters over the concentration range of 10-500 grams of solute/100 ml of solvent (ca. 0.1 - 5.0 Molar); the results are presented in Figures 1 and 2, pages 7 and 8.

The most conductive solution was formed with methyl formate, having a value of $3.2 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at a concentration of 30 grams of LiClO_4 /100 ml of solvent. For the other esters, the maximum conductivity of the LiClO_4 solution decreased with increasing molecular weight of the solvent.

3.1.2. Solubility of Various Salts in Ethyl Acetate

Attempts were made to dissolve other salts in ethyl acetate, those being AlCl_3 , AlF_3 , LiCl , LiI , KI , and KSCN . In all cases, the solubility was less than 0.2 grams/100 ml of solvent; and the specific conductance of the saturated solutions was less than $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$.

3.1.3. Stability of the Lower Esters in Presence of Metallic Lithium

Stability of the esters was studied by immersing lithium metal in both the pure solvent, and in solutions of LiClO_4 in the solvent. These systems were allowed to stand at room temperature in closed test tubes, and

FIGURE 1

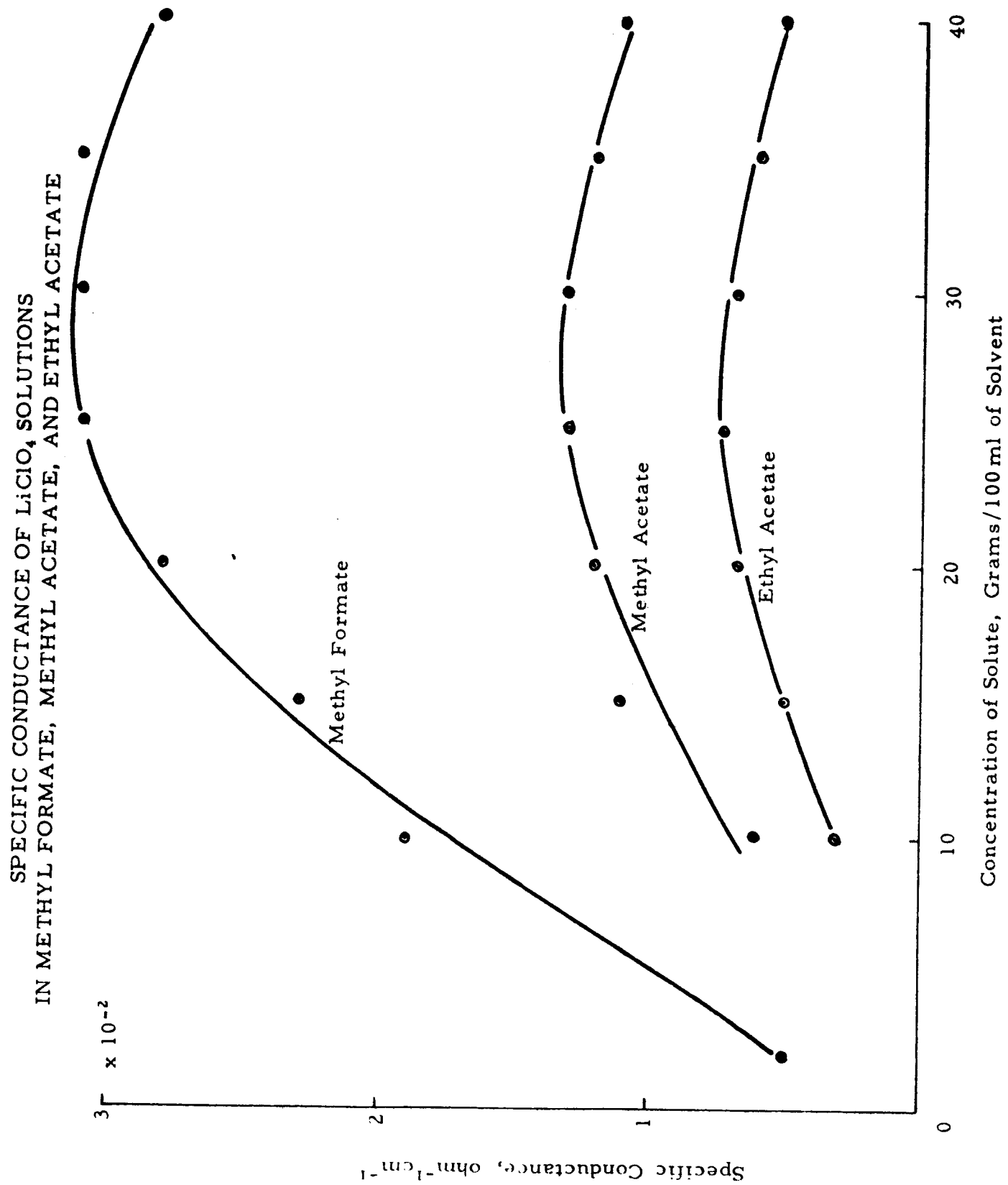


Figure 2

SPECIFIC CONDUCTANCE OF LiClO_4 SOLUTIONS
IN N-BUTYL FORMATE AND ETHYL ACETOACETATE

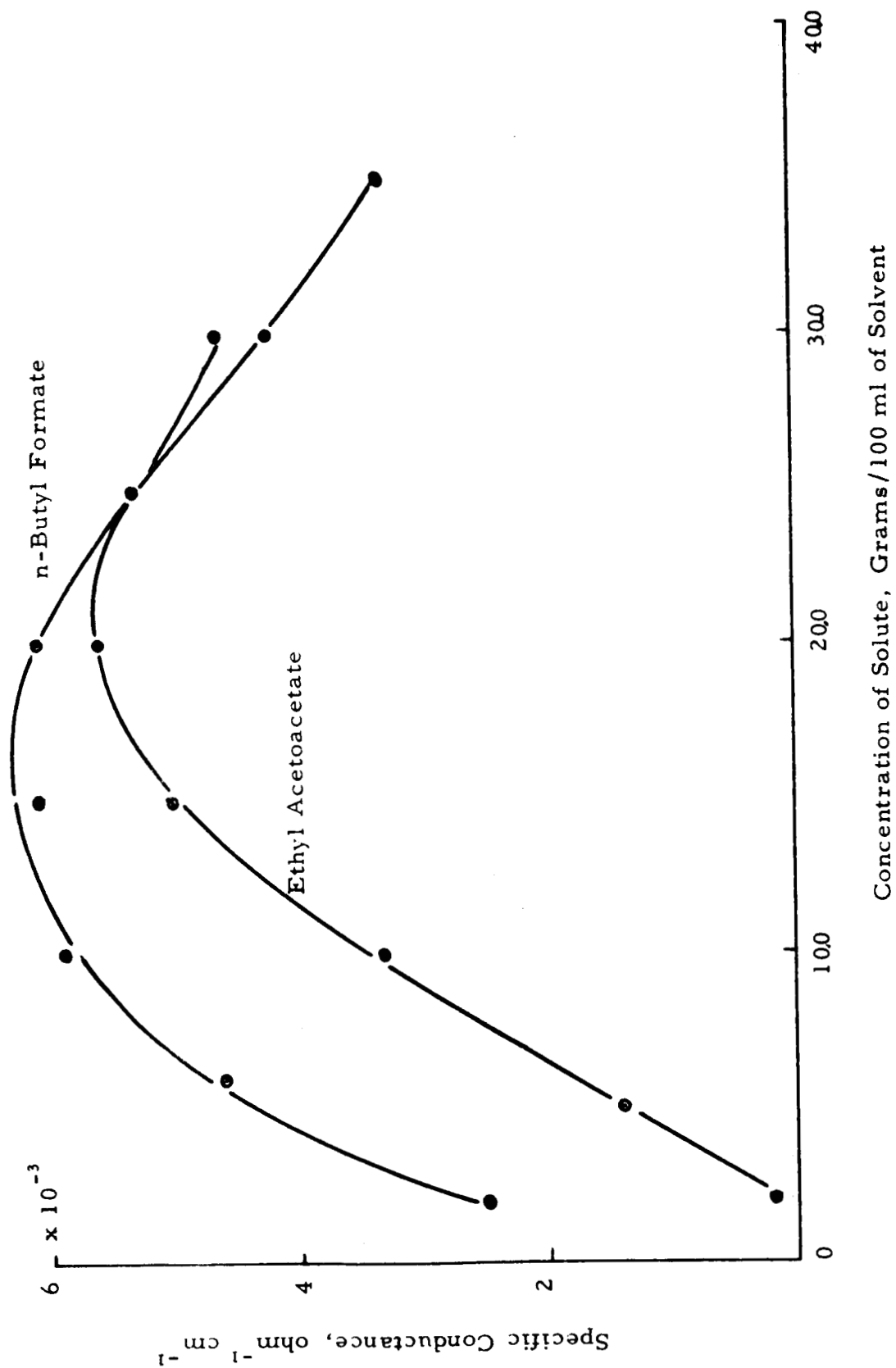
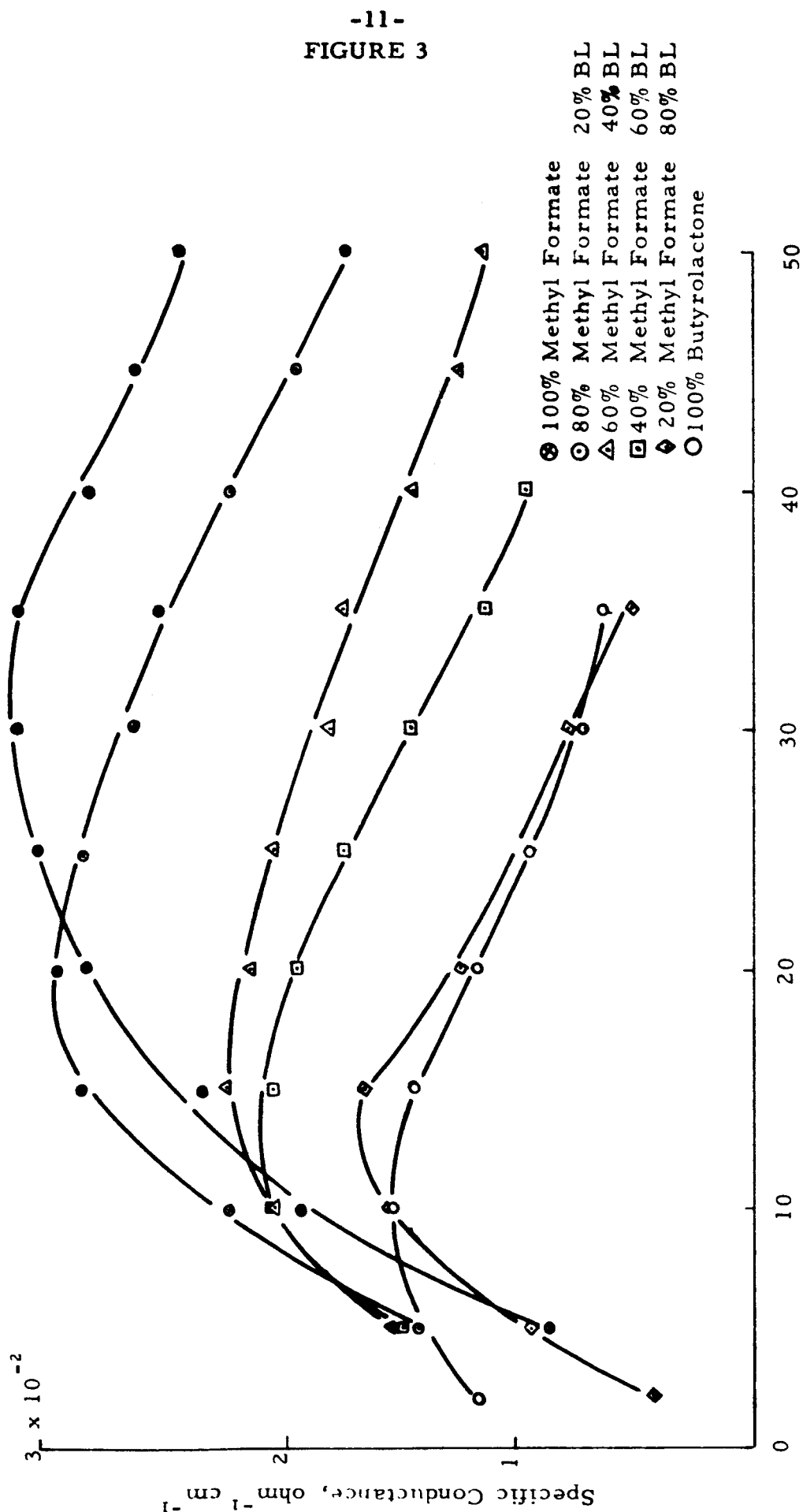


TABLE II

RESULTS OF LITHIUM STABILITY TESTS

<u>SOLVENT</u>	<u>LITHIUM STABILITY</u>	
	<u>SOLVENT ONLY</u>	<u>LiClO₄ SOLUTION</u>
Methyl Formate	Slow gas evolution on Li surface, inhibited by stoppering of test tube. White deposits are formed.	Same as with no solute present.
Methyl Acetate	Same as the above, except that stoppering of test tube appeared to stop gas evolution.	Gassing more rapid than without solute.
Ethyl Formate	Discoloration of liquid in 48 hours (yellow); brown deposit on Li.	No Test
Ethyl Acetate	Yellow deposit on Li after 24 hours	Yellow deposit on Li in 12 hours.
n-Butyl Formate	No visible reaction products after 5 days	Rapid reaction, heavy discoloration after 30 minutes.
Butyl Butyrate	Yellow deposit on Li after 24 hours.	No Test
Ethyl Acetoacetate	Immediate reaction; mixture gelled after 30 minutes.	No Test

SPECIFIC CONDUCTANCE OF SOLUTIONS OF LiClO_4
IN BUTYROLACTONE-METHYL FORMATE MIXTURES



Concentration of Solute, Grams of LiClO_4 /100 ml of Solvent Mixture

Solutions of LiClO_4 in acetone had the highest conductivity ($5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$) of all organic electrolytes tested in this laboratory. However, the solvent is sufficiently unstable in presence of lithium metal to make discharges longer than about the ten-hour rate impractical. Hence, a different anode material would be necessary in an acetone electrolyte cell.

The relative electrode potentials in acetone were measured for lithium, calcium, magnesium, aluminum, zinc, and copper by immersing the metals in a 1.4 M LiClO_4 -acetone solution and measuring the potential difference. The sample of lithium was supported on expanded nickel screen; the other metals were used without support. The potentials were measured with an 11-megohm VTVM and were found to be reproducible using various combinations of the electrodes. The potential values measured in this test are shown in Table III.

TABLE III

Metal Electrode Potentials in Acetone
Electrolyte: 1.4 M LiClO_4

<u>Electrode</u>	<u>Potential</u>
Ni/ Li	0
Ca	+0.7
Mg	+2.0
Al	+2.3
Zn	+2.8
Cu	+3.3

3.1.6. Comparison of Aqueous Electrode Potentials with Potentials in Other Solvents

To date, relatively little is known about electrode potentials in non-aqueous solutions. Plots comparing various non-aqueous oxidation potentials to standard aqueous potentials were made and are presented in Figures 4a to 4f starting on page 14.

Figure 4a is a plot of oxidation potentials in liquid ammonia as provided by Jolly¹ versus the standard aqueous oxidation potentials from Latimer.² It appears from Figure 4a and the succeeding five figures³ that electrode reactions of the elements may be separated into two categories, each of which constitutes a linear relationship. Copper, lead, silver, and mercury show some indication of shifting from Category A to Category B, depending upon the solvent in question. The two linear relations tend to converge in the region of the alkali and alkaline earth metals. Tentatively, it would appear that many of the electrode potentials in a solvent might be predicted with reasonable accuracy from a knowledge of the potential of lithium in the same solvent as indicated by line A of Figure 4a (the normal hydrogen electrode is considered at zero potential in both solvents). The potentials of the alkaline earths and the halogens (line B, Figure 4a) would appear at this time to require a knowledge of two potentials within the group; since H₂ with zero potential does not fall on this line.

¹Journal of Chemical Education, Volume 33, No. 10 (October 1956) p. 514.

²Wendell M. Latimer, Oxidation Potentials, Second Edition (1952).

³Roger Parsons, Handbook of Electrochemical Constants (1959) p. 73.

Figure 4a

AMMONIA OXIDATION POTENTIAL

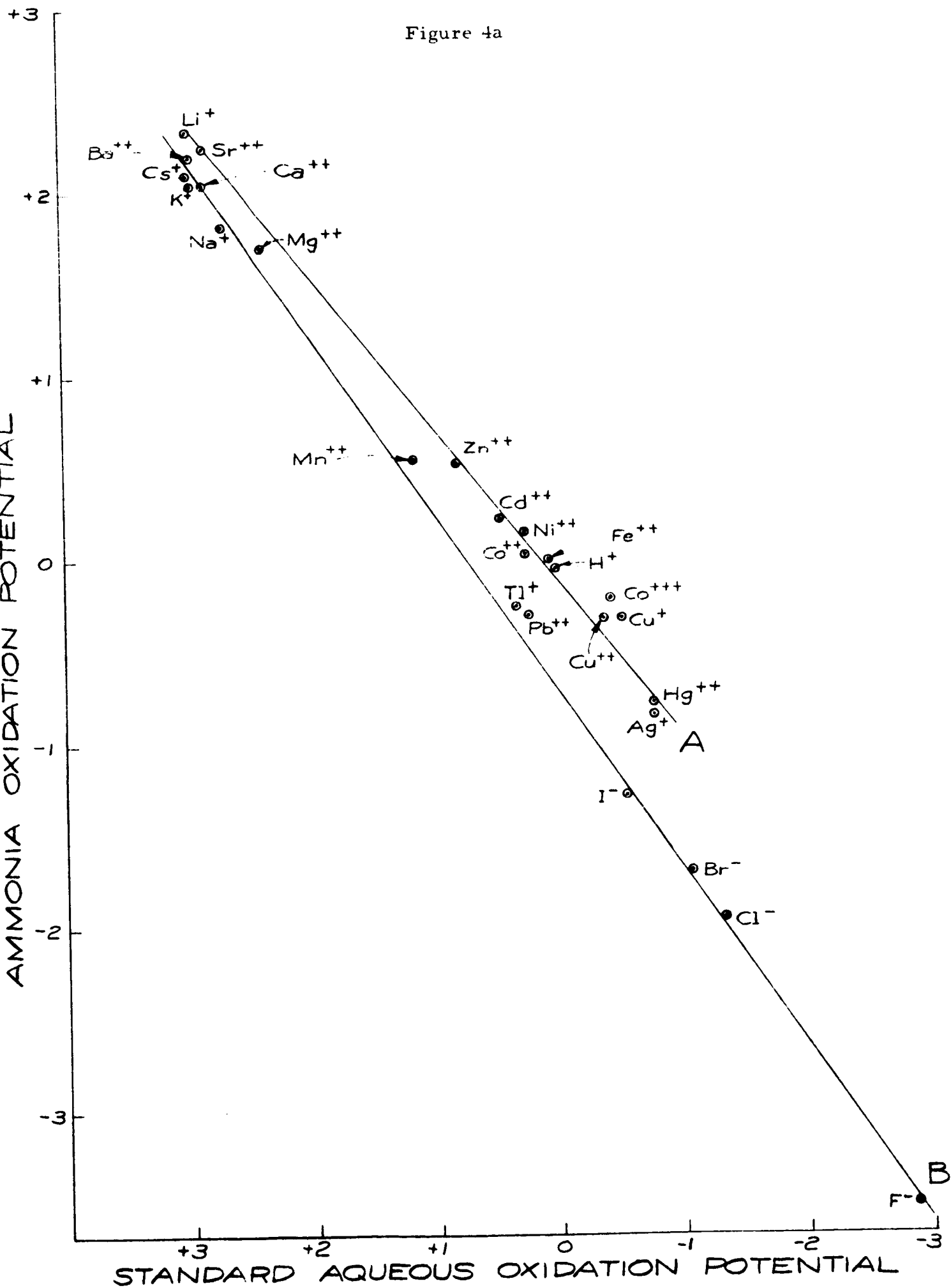


Figure 4b

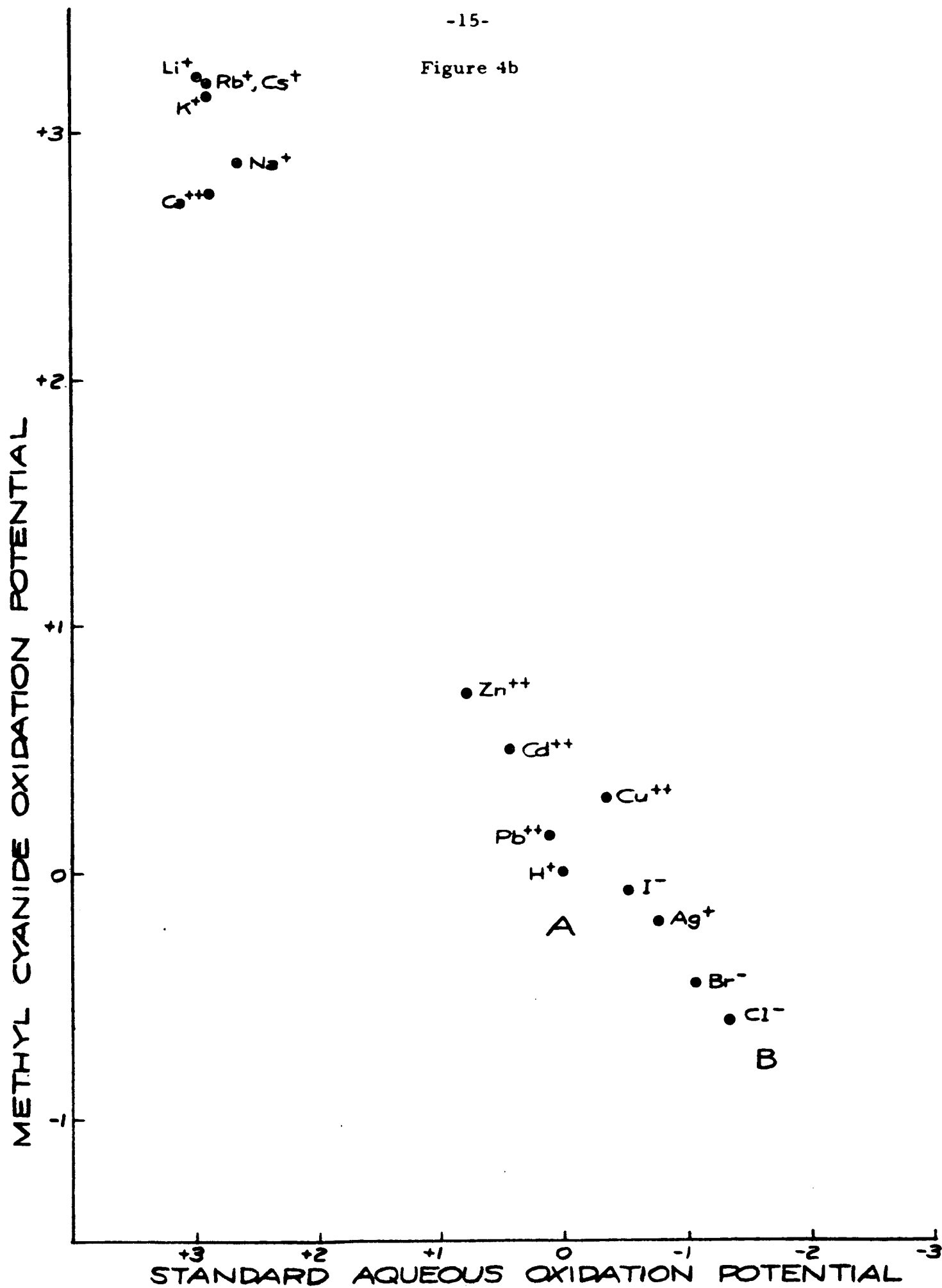


Figure 4c

METHYL ALCOHOL OXIDATION POTENTIAL

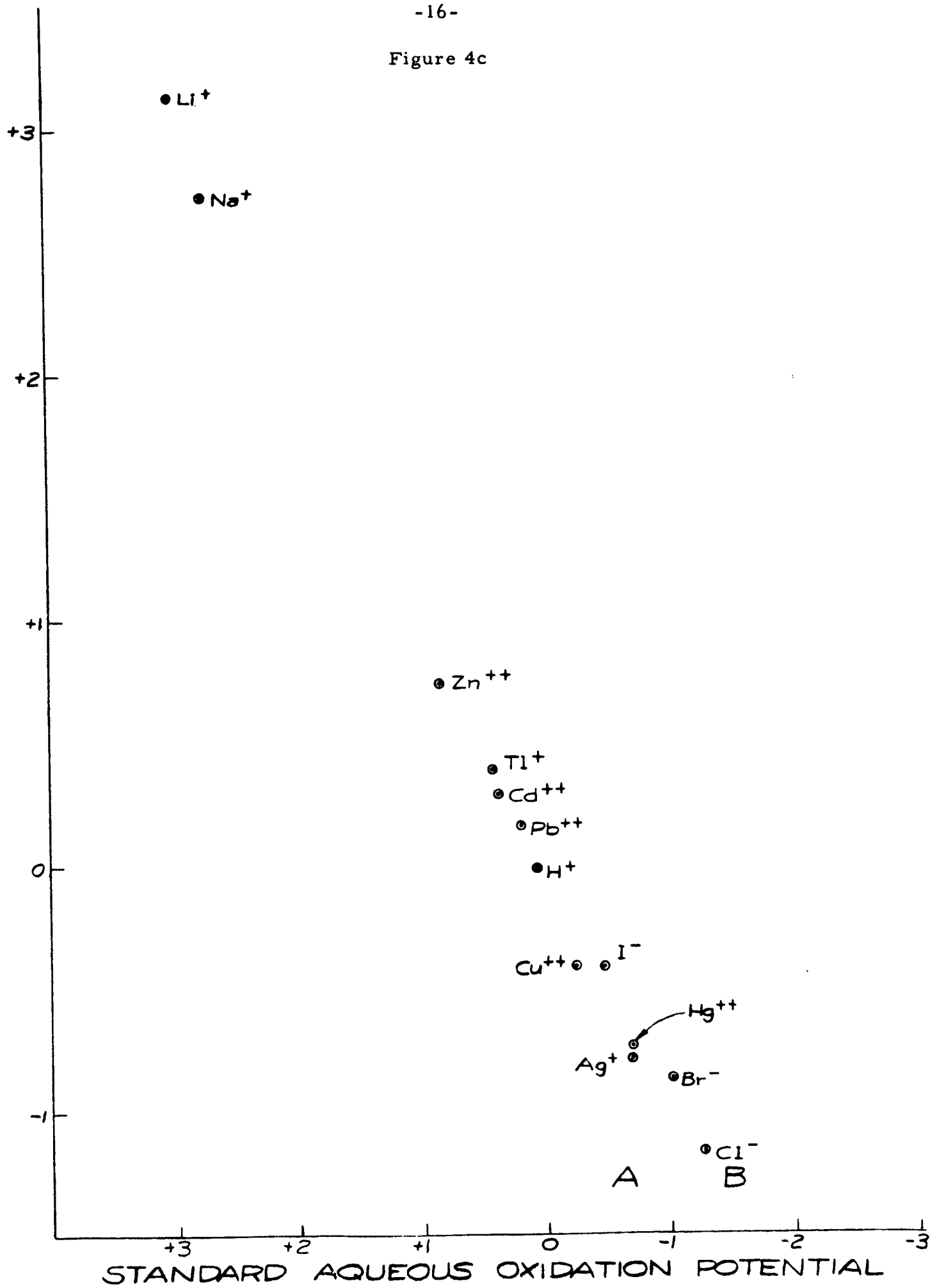


Figure 4d

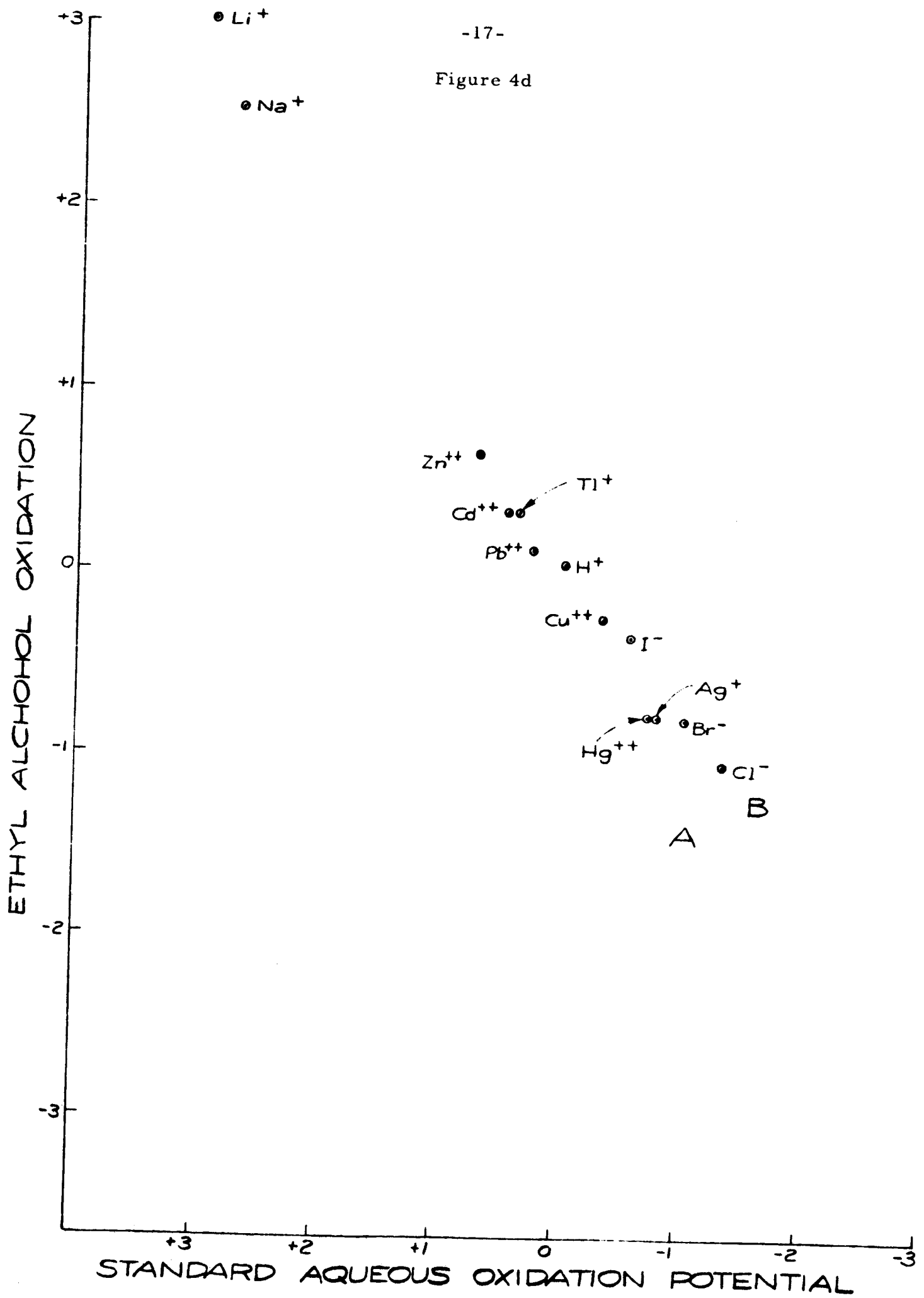


Figure 4e

FORMAMIDE OXIDATION POTENTIAL

Rb⁺ K⁺

Zn⁺⁺

Cd⁺⁺

Tl⁺

Pb⁺⁺

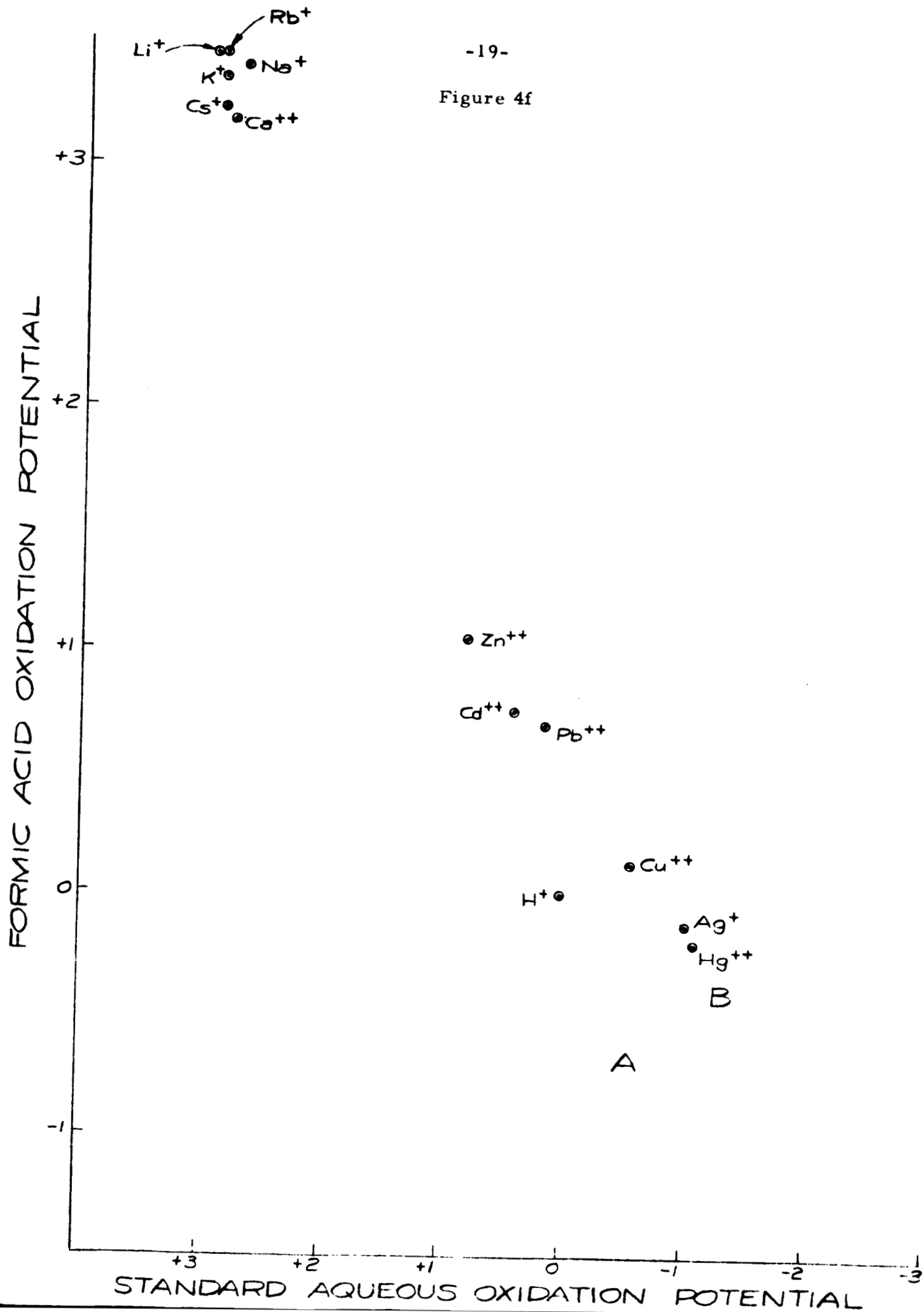
H⁺

Cu⁺⁺

A

STANDARD AQUEOUS OXIDATION POTENTIAL

Figure 4f



3.2. CELL SYSTEMS STUDIES

Three-plate prismatic (flat) cells having an electrode area of about 30 cm² were constructed and tested for discharge characteristics. Some of the cells were designed for the study of cathode efficiency and had a large excess of negative capacity. These cells are designated "experimental" and have the prefix "E" in the numbering sequence. Other cells were designed to study their performance with balanced electrode capacities, and had theoretical cathode capacities approximately equivalent to that of the two anodes. These cells are designated "laboratory," and have the prefix "L" in the numbering sequence.

3.2.1. Electrode Construction

The lithium negatives were constructed by pressing strips of the metal having a thickness of 1/16 inch onto expanded nickel support at about 100 pounds per square inch. The active material weight was 0.5 grams giving a theoretical capacity of 3.8 AH for the two anodes.

The cathode active material was prepared by several methods. The largest number of electrodes were built with material prepared by dry-mixing carbon, paper pulp, and the active material in a weight ration of 1:1:12. This material was placed in a steel mold together with an expanded nickel support and compressed at 250 - 1,000 pounds per square inch.

A modification of the above cathode construction consisted of mixing the carbon, paper, and active material with perchloroethylene, pressing the wet pad between filter papers at about 10 pounds per square inch

and vacuum drying. Water was used as the mix vehicle in building MnO_2 and other easily dried cathodes; the resulting mix was pressed and vacuum-dried as with perchloroethylene mix.

Finely divided polyethylene (Microthene) and a soluble resin (Gantrez 119) were ball-milled with carbon and the active material, and plates were made by pressing or sintering the mix onto the expanded metal support. Only initial studies in this type of construction have been performed to date.

3.2.2. Cell Construction

The three-plate, outside negative test cells were constructed as shown in Figure 5, page 22. The negatives were always assembled with the nickel-free side of the electrode facing the positive, since, in earlier tests, shorting through the separation between the anode and the cathode at the locations where the negative support was exposed to the positive had occurred.

Separation in all cells was vacuum dried "Efficiency No. 1698" blotter paper, which has a thickness of 0.025 inch. The assembled element was heat-sealed in a polyethylene envelope and supported vertically between blocks of wood in a test rack.

3.2.3. Discharge Tests

The majority of the discharges were performed at constant current, cell voltages being monitored continuously by a strip chart voltmeter (Brown "Elektronik"). The runs were made at room temperature, except for some cells having methyl formate as the electrolyte solvent,

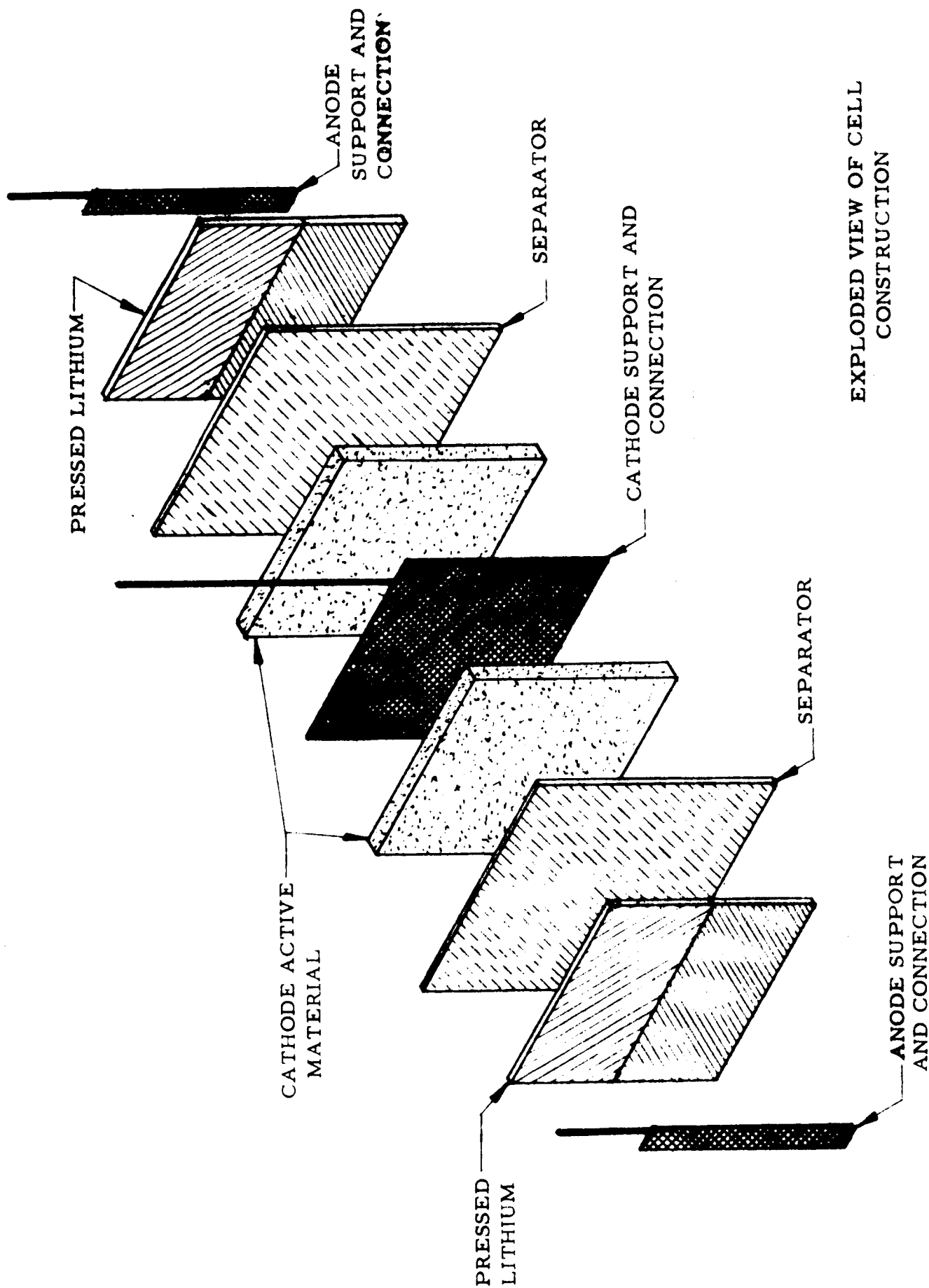


FIGURE 5

which were run at lowered temperatures (5°C - 40°C) in order to avoid rapid vaporization of the solvent.

The cells were activated via a hypodermic needle. After recording open-circuit potential, the discharge was started within one hour from addition of the electrolyte. The lateral compression of the cells was increased by introducing spacers in the assembly until discharge voltage showed no change with increasing compression. In most cells, this was achieved with light force applied by hand (measurements of the lateral force required were not obtained).

At the end of the discharge (usually at 0 volt), the cells were disassembled and the components were inspected.

3.2.4. Cell Discharge Results

The results of the discharge tests are summarized in Tables IV and V, pages 27 to 38; and a code for the abbreviations used in these tables is given on page 26.

The anode and cathode capacities listed in the tables are based on complete oxidation and reduction of the available active materials; in the case of sulfur, reduction to sulfide ion is assumed.

The electrolyte solutions listed were at a concentration giving optimum conductivity for the system. With methyl formate, the concentration of LiClO_4 solutions was 2.2 M, while in butyrolactone it was 1.5 M.

Special modifications to cathode construction, electrolyte composition, or cell construction are given in the "Remarks" column of

the tables. This column also lists discharge temperature if different from room temperature, open circuit stand time before discharge when longer than one hour, and, for some cells, electrochemical efficiency expressed in percent of total theoretical cathode capacity, and watt hours per pound of total cell weight.

To date, cell capacity studies have been mainly of an exploratory nature. Evaluation of the effect of construction factors on discharge characteristics is still affected by a lack of reproducibility of cell performance.

Electrochemical efficiency of up to 100 per cent was demonstrated with the paper-carbon cathode construction ($\text{NiF}_2 \cdot 4\text{H}_2\text{O}$ in acetone) at about the 10-day discharge rate. Efficiency of CuF_2 cathodes was as high as 70 per cent in methyl formate. In butyrolactone, this figure did not exceed 30 per cent, although values of over 50 per cent have been obtained in earlier work. The thickness of the cathode did not appear to affect discharge efficiency, the 8-gram cathodes showed an efficiency similar to that of the 3-gram plates. Also, capacity did not appear to depend on the discharge rate over the 40 to 250 hour range.

At the present, the CuF_2 cells with methyl formate electrolyte are yielding the highest watt hours per pound figures; also, they show the lowest polarization with load. The utility of this system appears to be limited; however, by the action of the solvent on the lithium anode and by the apparent solubility of the cathode material in the electrolyte, to a delayed action type of application.

The discharge characteristics of the CuF_2 -Li system at room temperature with methyl formate electrolyte is shown in Figure 6, page 39;

the effect of lowered temperature on the system is shown in Figure 7, page 40. The shape of the discharge curve is characteristic of dry-mix CuF_2 cathodes and the MF solvent at the discharge rate employed. The energy density for the cell illustrated in Figure 6 was 130 watt hours per pound of total cell weight, which, to date, is the highest figure obtained on the present program.

CODE TO TABLES IV AND V

PP	- Paper Pulp
BP	- Blotter Paper
MPR	- Microporous Rubber
PVC	- Polyvinyl Chloride
PE	- Polyethylene
MF	- Methyl Formate
BL	- Butyrolactone
AC	- Acetone
MP	- n-Methyl 2-Pyrrolidone
DMSO	- Dimethyl Sulfoxide
EA	- Ethyl Acetate
BF	- Butyl Formate
K-DIC	- Potassium Dichloroisocyanurate
TICA	- Trichloroisocyanuric Acid
Na-DIC	- Sodium Dichloroisocyanurate

TABLE IV
SUMMARY OF

Cell No.	CATHODE				ANODE			SEPARATION	
	Active Material	Binder	Wt. of mix, gm.	Theoretical A.H.	Material	Wt. of Li, gm.	A.H.	Material	Thickness, mm
E- 1	CuCl ₂	PP	3.0	1.02	Li	1.0	3.8	BP	0.6
E- 2	CuCl ₂	PP	3.0	1.02	Li	1.0	3.8	BP	0.6
E- 3	CuCl ₂	PP	3.0	1.02	Li	1.0	3.8	BP	0.6
E- 4	CuCl ₂	PP	3.0	1.02	Li	1.0	3.8	BP	0.6
E- 5	CuCl ₂	PP	3.0	1.02	Li	1.0	3.8	BP	0.6
E- 6	CuCl ₂	PP	3.0	1.02	Li	1.0	3.8	BP	0.6
E- 7	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E- 8	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E- 9	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-10	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-11	CuCl ₂	PE	3.5	1.19	Li	1.0	3.8	BP	0.6
E-12	CuCl ₂	PE	3.5	1.19	Li	1.0	3.8	BP	0.6
E-13	CuCl ₂	PE	3.5	1.19	Li	1.0	3.8	BP	0.6
E-14	CuF ₂	PP	3.5	1.58	Li	1.0	3.8	BP	0.6
E-15	CuF ₂	PP	3.5	1.58	Li	1.0	3.8	BP	0.6
E-16	CuF ₂	PP	3.5	1.58	Li	1.0	3.8	BP	0.6
E-17	CuF ₂	PP	3.5	1.58	Li	1.0	3.8	BP	0.6
E-18	CuF ₂	PP	3.5	1.58	Li	1.0	3.8	BP	0.6
E-19	CuF ₂	PP	3.5	1.58	Li	1.0	3.8	BP	0.6
E-20	K-DIC	PP	1.0		Li	1.0	3.8	BP	0.6

"EXPERIMENTAL" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Solute	Volume, cc	Open Circuit Potential	Load, ma	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A. H. / to Final Voltage	
BL	LiClO ₄	4.4	3.6	25	2.8	0	4.6		
BL	LiClO ₄	4.4	3.5	25	2.8	0	4.1		
EA	LiClO ₄	4.0	3.4	25	2.8	0	5.3		
EA	LiClO ₄	4.0	3.4	25	3.0	0	5.1		
MF	LiClO ₄	4.2	3.2	25	2.8	0	9.8		Solvent loss
MF	LiClO ₄	4.2	3.2	25	2.8	0	6.2		Solvent loss
BL	LiClO ₄	5.0	3.6	25	3.4	0	12.3		23% cathode efficiency
BL	LiClO ₄	5.0	3.6	25	3.4	0	15.1	0.38	28% cathode efficiency
EA	LiClO ₄	5.0	3.7	25	3.4	0	22.0	0.55	41% cathode efficiency
EA	LiClO ₄	5.0	3.7	25	3.4	0	22.0	0.55	41% cathode efficiency
BL	LiClO ₄	4.0	3.2	10	1.8	0	3.5		Pos. sintered at 350° F.
BL	LiClO ₄	4.0	3.2	10	1.8	0	0.7		Pos. sintered at 350° F.
BL	LiClO ₄	4.0	3.2	10	2.6	0	8.8		Pos. sintered at 350° F.
BL	LiClO ₄	5.0	3.6	25	3.2	0	6.0		
BL	LiClO ₄	5.0	3.5	25	3.2	0	8.4		a. m. : PP:C = 24:3:1
BL	LiClO ₄	5.0	3.5	25	2.9	0	8.4		
BL	LiClO ₄	5.0	3.5	25	2.8	0	8.8		a. m. : PP:C = 24:3:1
MF	LiClO ₄	5.0		10	0.8	0.	18		-40° C
MF	LiClO ₄	5.0		10	2.4	0.	15		Solvent loss
BL	LiClO ₄	10.0	4.1	25	3.5	0	5.2		

TABLE IV
SUMMARY OF

Cell No.	CATHODE				ANODE			SEPARATION	
	Active Material	Binder	Wt. of mix, gm.	Theoretical A.H.	Material	Wt. of Li, gm.	A.H.	Material	Thickness, mm
E-21	TICA	PP	3.0		Li	1.0	3.8	BP	0.6
E-22	S	PP	3.0	3.13 ¹	Li	1.0	3.8	BP	0.6
E-23	TICA	PP	3.0		Li	1.0	3.8	BP	0.6
E-24	AlF ₃	PP	4.0	4.30	Li	1.0	3.8	BP	0.6
E-25	Na-DIC	PP	4.0		Li	1.0	3.8	BP	0.6
E-26	CuS	PP	5.0	1.97	Li	1.0	3.8	BP	0.6
E-27	CuS	PP	5.0	1.97	Li	1.0	3.8	BP	0.6
E-28	S	PP	4.5	3.50 ¹	Li	0.5	1.9	BP	0.6
E-29	Hg ₂ SO ₄	PP	2.5	0.19	Li	0.5	1.9	BP	0.6
E-30	MnO ₂	PP	5.0	1.08	Li	1.0	3.8	BP	0.6
E-31	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-32	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-33	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-34	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-35	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-36	CuF ₂	PP	3.0	1.35	Li	1.0	3.8	BP	0.6
E-37	CuS	PP	3.8	1.51	Li	1.0	3.8	BP	0.6
E-38	mDNT	PP	2.0	0.13	Li	1.0	3.8	BP	0.6
E-39	CuF ₂	PP	4.5	2.04	Mg	1.6	3.2	BP	0.6
E-40	NiF ₂ ·4H ₂ O	PP	4.0	1.03	Li	1.0	3.8	BP	0.6

Continued

"EXPERIMENTAL" CELL DATA

ELECTROLYTE			DISCHARGE					A. H. /to Final Voltage	REMARKS
Solvent	Solute	Volume, cc	Open Circuit Voltage	Load, ma	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.		
EA	LiClO ₄	8.0	4.1	5	3.1	2.0	4.0		Pos. grid (Ni) corroded
EA	LiClO ₄	8.0	3.3	15	2.6	0	13.0	0.22	
EA	LiClO ₄	8.0	4.1	15	3.1	0	17.0		Pos. grid (Cu) corroded
BL	LiCl	8.0	2.6	5	2.3	0.3	22.0	0.11	
BL	KSCN	8.0	4.1	5	3.3	0	13.0		Pos. grid (Ni) corroded
BL	KSCN	8.0	2.9	25	2.6	0	7.0	0.17	
BL	KSCN	8.0	2.9	25	2.6	0	9.0	0.22	
BL	LiClO ₄	8.0	2.6	5	2.6	0	44.0	0.22	
BL	LiClO ₄	6.0	3.4	5	3.1	0.3	37.0	0.18	95% cathode efficiency
BL	LiClO ₄	8.0	2.9	5	3.0	0	20.0	0.10	
MF	LiClO ₄	5.0	3.6	25	3.3	1.7	37.5	0.94	70% cathode efficiency
MF	LiClO ₄	5.0	3.6	25	3.3	0.7	37.5	0.94	70% cathode efficiency
BF	LiClO ₄	5.0	3.6	10	3.0	0	14.1		
BF	LiClO ₄	5.0	3.6	25	3.1	0.7	14.0		
MF	LiClO ₄	5.0	3.3	5	3.2	0.7	192.0	0.96	Test. temp.: -40° C.
MF	LiClO ₄	5.0	3.3	5	3.2	1.4	192.0	0.96	Test. temp.: -40° C.
BL	LiClO ₄	9.0	3.0	5	2.6	0	107.0	0.53	35% cathode efficiency
BL	LiClO ₄	6.0		2	2.2	1.7	13.5		
AC	MgClO ₄	6.0	1.5	25	1.5	0.6	17.0	0.42	
BL	LiClO ₄	6.0	2.9	10	2.5	0	37.8	0.38	37% cathode efficiency

TABLE IV
SUMMARY OF

Cell No.	C A T H O D E				A N O D E			S E P A R A T O R	
	Active Material	Binder	Wt. of mix, gm.	Theoretical A.H.	Material	Wt. of Li, gm.	A. H.	Material	Thickness, mm
E-41	NiF ₂ ·4H ₂ O	PP	4.0	1.03	Li	1.0	3.8	BP	0.6
E-42	NiF ₂ ·4H ₂ O	PP	4.0	0.76	Li	1.0	3.8	BP	0.6
E-43	HgCl ₂	PP	10.0	1.34	Mg	2.0	4.1	BP	0.6
E-44	HgCl ₂	PP	5.0	0.79	Zn	6.6	5.4	BP	0.6
E-45	HgCl ₂	PP	5.0	0.79	Mg	2.0	4.1	BP	0.6
E-46	NiF ₂ ·4H ₂ O	PP	5.0	1.29	Zn	6.6	5.4	BP	0.6
E-47	NiF ₂ ·4H ₂ O	PP	4.0	1.03	Mg	2.0	4.1	BP	0.6
E-48	NiF ₂ ·4H ₂ O	PP	4.0	1.03	Ca			BP	0.6
E-49	CuCl ₂	PP	5.0	1.60	Zn	6.6	5.4	BP	0.6
E-50	AgO	PP	5.0	1.73	Li	1.0	3.8	BP	0.6
E-51	CuCl ₂	PP	4.0	1.28	Li	0.5	1.9	BP	0.6
E-52	CuCl ₂	PP	4.0	1.28	Li	0.5	1.9	BP	0.6
E-53	CuCl ₂	PP	4.0	1.28	Li	0.5	1.9	BP	0.6
E-54	CuF ₂	PP	4.0	1.83	Li	1.0	3.8	BP	0.6
E-55	CuF ₂	PE	3.7	1.87	Li	1.0	3.8	BP	0.6
E-56	NiF ₂ ·4H ₂ O	PE	2.9	0.80	Li	1.0	3.8	BP	0.6
E-57	MnO ₂	PP	8.0	1.73	Zn	6.6	5.4	BP	0.6
E-58	MnO ₂	PP	8.0	1.73	Li	1.0	3.8	BP	0.6
E-59	MnO ₂	PP	8.0	1.73	Zn			PVC	0.74
E-60	Ni ₂ O ₃	PP	4.3	0.97	Li	1.0	3.8	BP	0.6

Continued

"EXPERIMENTAL" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Solute	Volume, cc	Open Circuit Potential	Load, ma	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A.H. /to.Final Voltage	
BL	LiClO ₄	6.0	3.0	10	2.6	0	39.4	0.39	4% Triton X100 in electrode
BL	LiClO ₄	6.0	3.0	10	2.7	0	13.2	0.13	4% Triton X100 in electrode
AC	LiClO ₄	7.0	1.6	25		0	17.8	0.42	
AC	MgClO ₄	10.0	1.0	25	0.9	0	5.0		
AC	MgClO ₄	7.0	2.0	25	1.7	0	4.0		~100% cathode efficiency
AC	MgClO ₄	10.0	0.7	5	0.3	0	260.0	1.30	~100% cathode efficiency
AC	MgClO ₄	10.0	1.2	5	0.9	0	212.0	1.06	
AC	MgClO ₄	10.0	2.3	5	1.6	1.8	5.0		Poor anode connection
AC	MgClO ₄	8.0	0.9	5	0.7	0	91.8	0.46	
BL	LiClO ₄	8.0	3.7	25	3.3	1.8	6.6		
BL	LiClO ₄	8.0	3.5	25	3.3	0	4.0		Solvent-mix cathode
BL	LiClO ₄	8.0	3.5	25	3.3	0	2.0		Solvent-mix cathode
BL	LiClO ₄	8.0	3.4	10	3.2	0	6.0		Solvent-mix cathode
MF	LiClO ₄	8.0		10	3.0	0	120.0	1.20	65% cathode: efficiency
MF	LiClO ₄	8.0		19.5	3.2	0.9	52.0	1.00	Test. temp.: +5° C.
MF	LiClO ₄	8.0		14	2.0	0.5	55.0	0.77	Test. temp.: +5° C. ³
H ₂ O	KOH	8.0		10	1.5	0	23.4		
BL	LiClO ₄	8.0		10	3.5	0	60.0	0.60	
H ₂ O	KOH	8.0	1.5	25	1.5	0	43.0	1.05	61% cathode efficiency
BL	LiClO ₄	7.0	2.5	10	2.1	0	13.2	0.13	

TABLE IV
SUMMARY OF

Cell No.	CATHODE				ANODE			SEPARATION	
	Active Material	Binder	Wt. of mix, gm.	Theoretical A.H.	Material	Wt. of Li, gm.	A.H.	Material	Thickness, mm
E-61	MnO ₂	PP	8.0	1.73	Li	1.0	3.8	BP	0.6
E-62	CoF ₂ · $\frac{1}{2}$ H ₂ O	PP	3.4	1.21	Li	1.0	3.8	BP	0.6
E-63	CoF ₂ · $\frac{1}{2}$ H ₂ O	PP	7.0	2.49	Li	1.0	3.8	BP	0.6
E-64	MnO ₂	PP	8.0	1.98	Li	1.0	3.8	BP	0.6
E-65	MnO ₂	PP	8.0	1.98	Li	1.0	3.8	BP	0.6

Continued

"EXPERIMENTAL" CELL DATA

ELECTROLYTE					DISCHARGE				REMARKS
Solvent	Solute	Volume, cc	Open Circuit Potential	Load, ma	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A.H. /to Final Voltage	
MP	LiClO ₄	10.0	3.7	10	3.2	0	134.6	1.35	78% cathode efficiency
MP	LiClO ₄	7.0	3.3	10	2.5	0	106.6	1.07	80% cathode efficiency
BL	LiClO ₄	10.0	3.2	10	2.9	0	67.8	0.68	
MF	LiClO ₄	6.0	3.7	100	2.8	0.5	22.5	2.25	100%+ cathode efficiency
MF	LiClO ₄	6.0		10		0.7	188.5	1.89	95% cathode efficiency

TABLE V
SUMMARY OF

Cell No.	C A T H O D E				A N O D E			S E P A R A T I O N	
	Active Material	Binder	Wt. of mix, gm.	Theoretical A.H.	Material	Wt. of Li, gm.	A.H.	Material	Thickness, mm
L-1	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-2	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-3	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-4	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-5	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-6	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-7	CuF ₂	PP	8.0	3.42	Li	1.0	3.8	BP	0.6
L-8	CuF ₂	PP	8.0	3.65	Li	1.0	3.8	BP	0.6
L-9	CuF ₂	PP	8.0	3.68	Li	1.5	5.7	BP	0.6
L-10	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-11	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-12	CuF ₂	PP	8.0	3.65	Li	1.0	3.8	BP	0.6
L-13	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-14	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-15	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-16	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-17	CuF ₂	PP	8.0	3.66	Li	1.0	3.8	BP	0.6
L-18	MnO ₂	PP	8.0	1.98	Li	1.0	3.8	BP	0.6
L-19	MnO ₂	PP	8.0	1.98	Li	1.0	3.8	BP	0.6
L-20	MnO ₂	PP	8.0	1.98	Li	1.0	3.8	BP	0.6

"LABORATORY" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Solute	Volume, cc	Open Circuit Potential	Load, ma	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A. H. /to Final Voltage	
MF	LiClO ₄	8.0	3.4	25	3.1	0.4	40.0	1.0	Solvent loss
MF	LiClO ₄	8.0		25	3.5	2.5	27.3		Solvent loss
MF	LiClO ₄	8.0		20	2.9	1.1	24.0	1.86	5°C
MF	LiClO ₄	8.0		10	3.2	0	92.4	0.92	-40°C
MF	LiClO ₄	8.0		25	3.0	0	40.5	1.01	-40°C
MF	LiClO ₄	8.0		25	3.0	0	67.0	1.67	Approx. 113 WH/# 5-plate cell: -40°C 123 WH/#
MF	LiClO ₄	8.0		25	3.3	1.2	40.0	1.00	
MF	LiClO ₄	8.0		21	3.2	1.3	96.0	2.02	
MF	LiClO ₄	8.0		25	3.2	0	76.0	1.90	
MF	LiClO ₄	8.0		10	3.0	1.2	230.0	2.30	
MF	LiClO ₄	8.0		25	3.1	0	64.0	1.60	130 WH/# 17 days o. c. stand
BL	LiClO ₄	8.0		10		0.4	74.0		
MF	LiClO ₄	8.0		51	3.2	1.5	40.5	2.06	
BL	LiClO ₄	8.0	3.44	10	2.0	0	3.8		
BL	LiClO ₄	8.0	3.46	10	2.5	1.5	7.0		
BL	LiClO ₄	8.0	3.44	10	2.5	1.4	7.0		17 days o. c. stand 14 days o. c. stand
BL	LiClO ₄	8.0	3.47	10	1.5	0	3.8		
BL	LiClO ₄	8.0	3.66	10	2.5	0	13.5		
BL	LiClO ₄	8.0	3.71	10	2.7	0	66.0		
BL	LiClO ₄	8.0	3.67	10	2.1	0	4.0		

TABLE V
SUMMARY OF

Cell No.	C A T H O D E				A N O D E			S E P A R A T I O N	
	Active Material	Binder	Wt. of mix, gm.	Theoretical A.H.	Material	Wt. of Li, gm.	A.H.	Material	Thickness, mm
L-21	MnO ₂	PP	8.0	1.98	Li	1.0	3.8	BP	0.6
L-22	CuF ₂	PP	7.5	3.23	Li	1.0	3.8	BP	0.6
L-23	CuF ₂	PP	7.5	3.23	Li	1.0	3.8	BP	0.6
L-24	CuF ₂	PP	7.5	3.23	Li	1.0	3.8	MPR	1.1
L-25	CuF ₂	PP	7.5	3.23	Li	1.0	3.8	MPR	1.1

Continued

"LABORATORY" CELL DATA

ELECTROLYTE			DISCHARGE						REMARKS
Solvent	Solute	Volume, cc	Open Circuit Voltage	Load, ma	Initial Closed Circuit Voltage	Final Closed Circuit Voltage	Time to Final Voltage, hrs.	A.H./to Final Voltage	
BL	LiClO ₄	8.0	3.64	10	2.5	0	39.0		14 days o.c. stand
BL	LiClO ₄	6.0	3.5	25	3.2	0	18.0		Solvent mix cathode
MF	LiClO ₄	10.0		25	2.9	1.5	50.	1.25	-40°C; 80 WH/lb.
BL	LiClO ₄	6.0		25	3.2	0	30.4		
DMSO	LiClO ₄	5.0		10	3.0	1.5	9.0		

Figure 6

DISCHARGE PROPERTIES OF Li-CuF₂ CELL
WITH 50-ohm LOAD AT ROOM TEMPERATURE

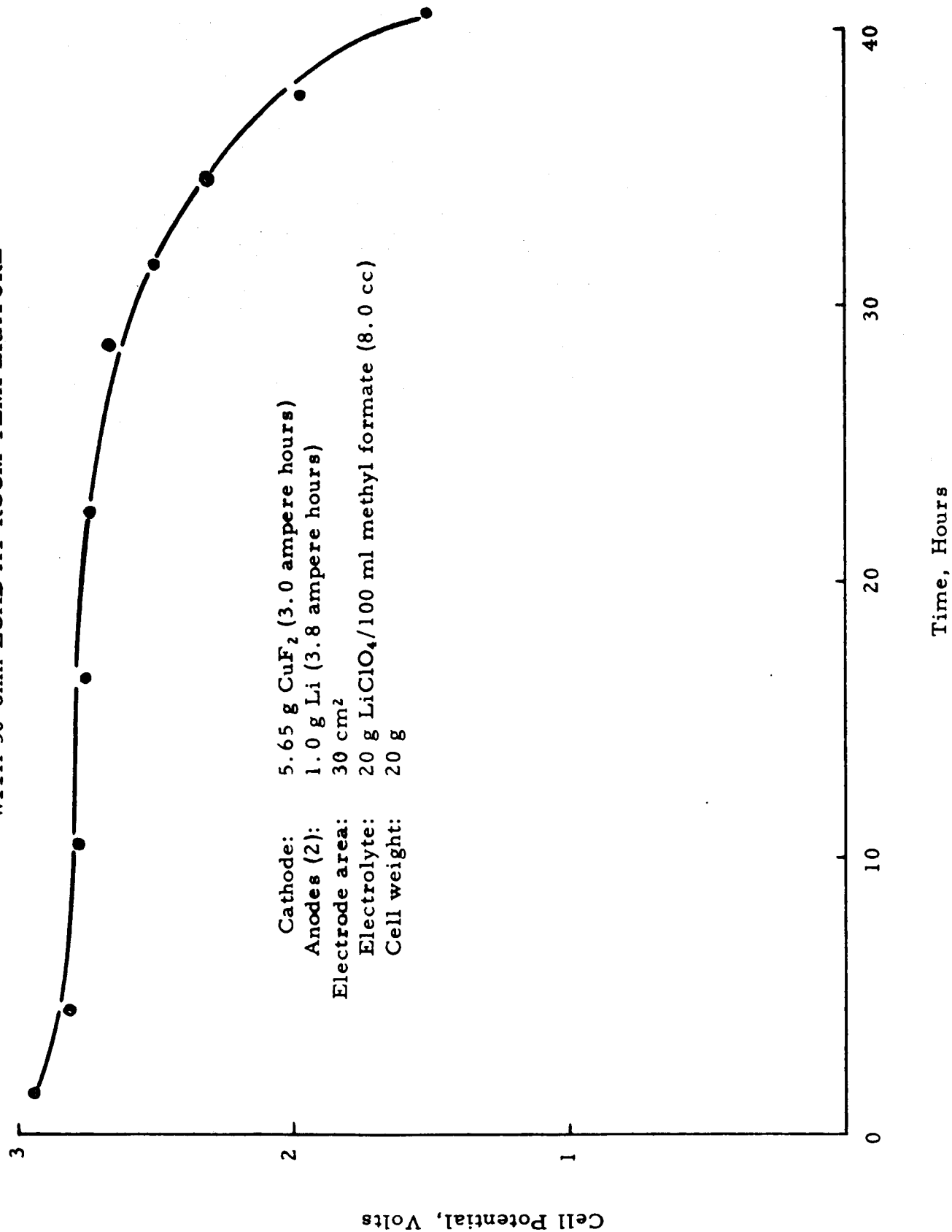
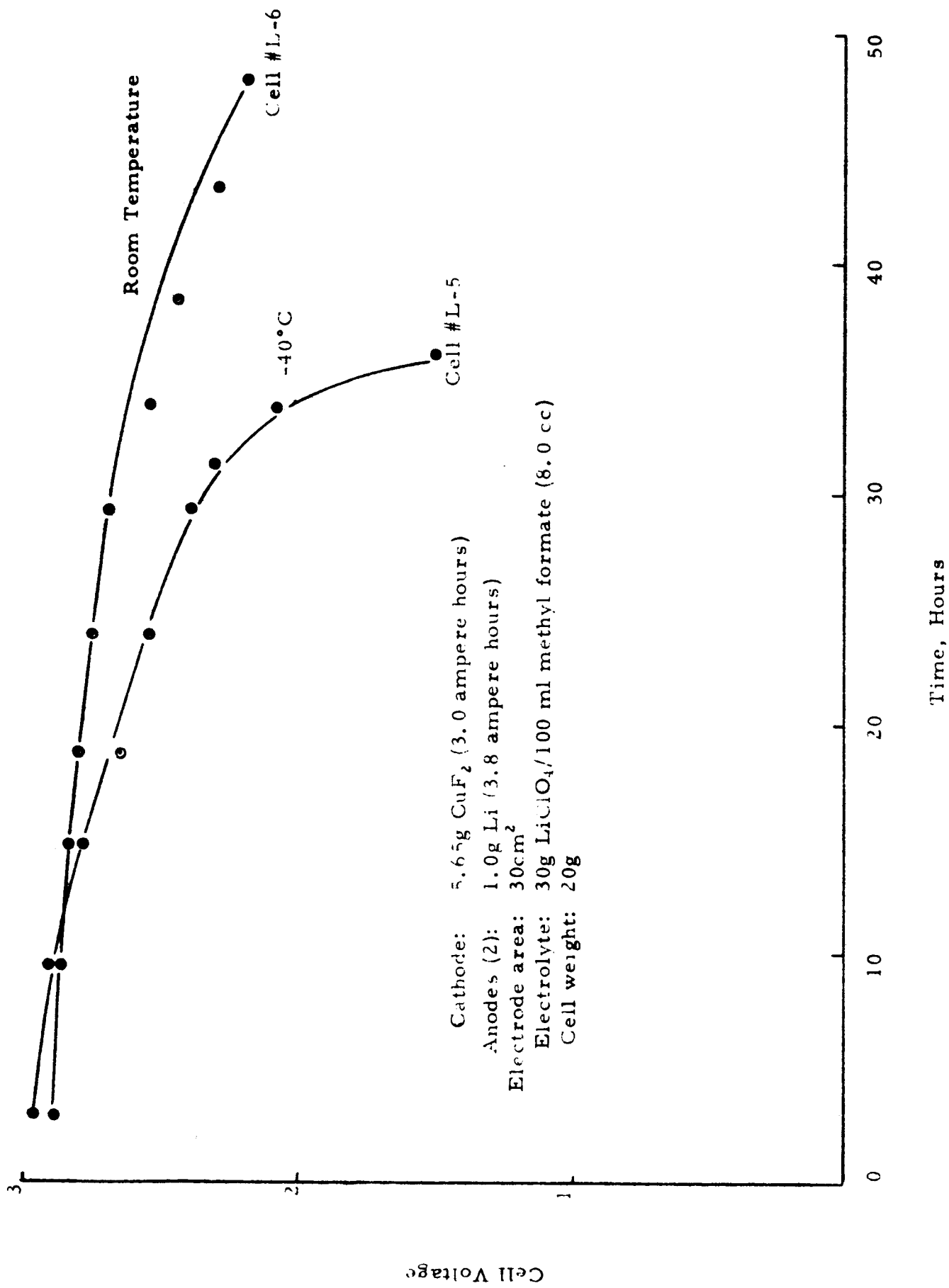


FIGURE 7



4. ACTIVITY PLANNED FOR THE SECOND QUARTER

Studies of electrolyte systems will continue with the objective of limiting the number of electrolytes for extensive cell studies to three or four of the most favorable systems. The criteria which will be applied to make the choice will include conductivity, resistance to decomposition, stability of lithium metal, and solubility of cathode materials in the solvent. Also, discharge performance of "experimental" cells having the optimum electrode construction available at the time, will be determined using the candidate electrolyte solvents before making a final choice of a system for "laboratory" cell tests.

Methods of producing higher efficiency positive electrodes will be studied extensively. Both copper fluoride and other possible cathode materials will be used in making test electrodes. Work on lower density paper-carbon electrodes using non-aqueous mix vehicles (such as kerosene) will continue. Other planned work includes construction and testing of sintered electrodes, and electrodes made with soluble binders. Test cells having reference electrodes will be constructed in order to study the effect of various construction variables on the degree of polarization of the positive and negative electrodes.

5. APPENDIX

ENERGY EFFICIENCY OF COMMERICAL PRIMARY SYSTEMS*

<u>Couple</u>	<u>Commercial WH/lb.</u>	<u>Max. Load Potential</u>	<u>Theoretical** WH/lb.</u>	<u>Percent Efficiency</u>
MnO ₂ -Zn	30	1.50	168	18
HgO-Zn	53	1.35	116	46
AgO-Zn	70	1.50	194	36
PbO ₂ -Zn	26	2.40	190	13.7
AgCl-Mg	30	1.60	125	24
CuCl-Mg	30	1.30	145	21
PbO ₂ -Pb	20	2.10	115	17.4

*Data from C. K. Morehouse, R. Glicksman, and G. S. Lozier, Proceedings of IRE, Volume 46, Number 8, August 1958.

**WH/lb. = (Max. load pot.) (F)/combined equivalent weight; electrolyte weight not included, one electron change for MnO₂.